

Unit 4: Rates, Equilibria and Further Organic Chemistry

Topic 11: Kinetics

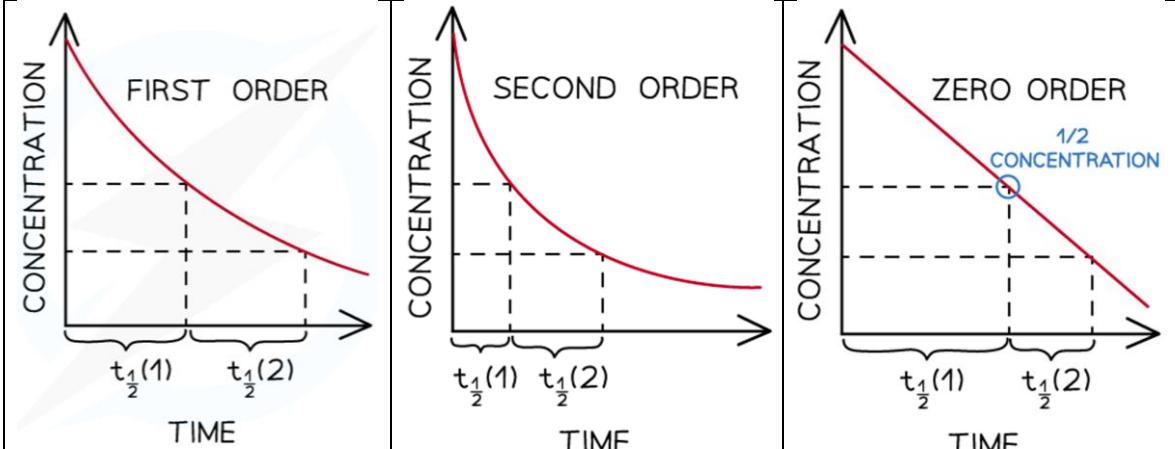
Knowledge of the concepts introduced in Unit 2, Topic 9A: Kinetics will be assumed and extended in this topic.

Students will be assessed on their ability to:

11.1	<p>understand the terms:</p> <ul style="list-style-type: none">i rate of reactionii rate equation, $\text{rate} = k[A]^m[B]^n$ where m and n are 0, 1 or 2iii order with respect to a substance in a rate equationiv overall order of a reactionv rate constantvi half-lifevii rate-determining stepviii activation energyix heterogeneous and homogeneous catalyst										
	<p>Rate of reaction is defined as the change (increase or decrease) in concentration of a species (product or reactant) in unit time. All reaction rates are positive, and its unit is $\text{mol dm}^{-3} \text{s}^{-1}$</p> $\text{Rate} = \frac{d[\text{product}]}{dt} \qquad \qquad \text{Rate} = -\frac{d[\text{reactant}]}{dt}$ <p>Rate equation expresses the mathematical relationship between the rate of reaction and the concentrations of the reactants</p> <p>For a reaction: $\text{A(aq)} + \text{B(aq)} \rightarrow \text{C(aq)} + \text{D(g)}$</p> <p>rate of reaction = $k[\text{A}]^m[\text{B}]^n$ where m and n are orders with respect to each reactant</p> <p>Order (of a reactant species) is the power to which the concentration of the species is raised to in the equation</p> <ol style="list-style-type: none">0. Zero order rate equation: rate = $k[\text{A}]^0$ or rate = k1. First order rate equation: rate = $k[\text{A}]$2. Second order rate equation: rate = $k[\text{A}]^2$3. Third order rate equation: rate = $k[\text{A}]^2[\text{B}]$ <table border="1" style="float: right; margin-right: 20px;"><tr><th>Order</th><th>Unit</th></tr><tr><td>Zero</td><td>$\text{mol dm}^{-3} \text{s}^{-1}$</td></tr><tr><td>First</td><td>s^{-1}</td></tr><tr><td>Second</td><td>$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$</td></tr><tr><td>Third</td><td>$\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$</td></tr></table> <p>Overall order of a reaction is the sum of all the individual orders of species</p> <p>Orders of reaction can only be determined experimentally</p> <p>Rate constant is k</p> <p>Every reaction has its own rate equation and rate constant</p> <p>Rate constants only change their value with a <i>change in temperature</i></p> <p>Half-life is the time taken for the concentration of any reactant to halve</p> <p>Rate-determining step is the slowest step in the mechanism for a reaction</p> <p>Activation energy is the minimum energy that the colliding particles must obtain to reach the energy level of the transition state. Once it has been reached, the particles can react to form the products and release energy as they do so</p>	Order	Unit	Zero	$\text{mol dm}^{-3} \text{s}^{-1}$	First	s^{-1}	Second	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Third	$\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$
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	<p>Heterogenous catalysts are in a different phase (solid, liquid, solution or gas) to that of the reactants</p> <p>Homogenous catalysts are in the same phase (solid, liquid, solution or gas) as the reactants</p>
11.2	be able to calculate the half-life of a reaction, using data from a suitable graph, and identify a reaction with a constant half-life as being first order
	<p>Half-life ($t_{1/2}$) is the time taken for the concentration of a reactant to halve</p> <ul style="list-style-type: none"> - Half-life is independent of concentration and all first order reactions have constant half-lives at a given temperature - If the half-life is short, the reaction is rapid/ If it is long, the reaction is slow
11.3	<p>be able to select and justify a suitable experimental technique to obtain rate data for a given reaction, including:</p> <ol style="list-style-type: none"> i titration ii colorimetry iii mass change iv volume of gas evolved v other suitable technique(s) for a given reaction
i	<p>Titration</p> <p>Small samples of known volume (aliquots) are removed from a reaction mixture at regular intervals, quenched (stopping or slowing down reaction by cooling or diluting) and then titrated against a known concentration of reagent to find the concentrations of known compounds in the aliquots</p> <p>A graph of concentration of reagent against time is plotted and the gradient at time t = 0 is measured to obtain initial rate</p> <p>$\text{HCOOCH}_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{HCOONa}(\text{aq}) + \text{CH}_3\text{OH}(\text{aq})$ The NaOH could be titrated with an acid</p> <p>$\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$ The H⁺ could be titrated with an alkali</p> <p>$\text{CH}_3\text{COCH}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_2\text{I}(\text{aq}) + \text{H}^+(\text{aq}) + \text{I}^-(\text{aq})$ The I₂ could be titrated with sodium thiosulphate</p>
ii	<p>Colorimetry</p> <p>For reactions where one of the reactants or products is colored then a colorimetry can be used to measure the change in color of the reacting mixtures</p> <p>A colorimeter measures the amount of light that passes through a solution</p> <p>Measure the transmittance / absorbance values of light passing through a solution at various times. One such example is the reaction between propanone and iodine:</p> $\text{H}_2\text{O}_2(\text{aq}) + 2\text{I}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})$ <p>The I₂ produced is a brown solution</p> <p>!Note that this method is not ideal for reactions that form precipitates</p>
iii	<p>Mass change</p> <p>The total mass of reaction mixture is measured as the reaction progresses using a digital balance</p> <p>One such example is the rate of reaction between calcium carbonate and hydrochloric acid, because as carbon dioxide escapes, mass decreases</p> <p>$\text{CaCO}_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$</p> <p>!Note that gas given off should have a relatively high density and is allowed to escape</p>

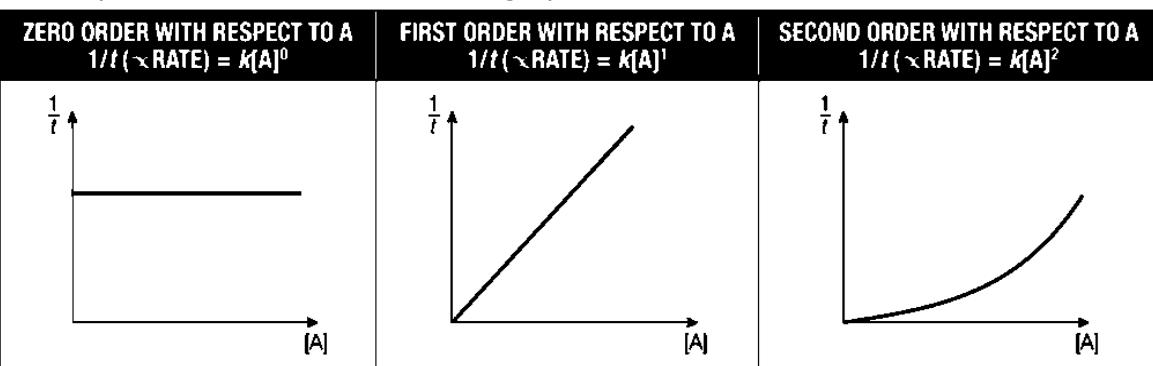
iv	<p>Volume of gas evolved</p> <p>There are two ways of doing this: collection over water into a measuring cylinder or collection using a gas syringe (generally more precise)</p> <p>One such example is the decomposition of hydrogen peroxide</p> <p>!Note that reactions producing gases soluble in water cannot use this technique</p>																									
v	<p>Electrical Conductivity</p> <p>The number and type of ions in a solution affect its electrical conductivity. As some chemical reactions take place in solution, the ionic balance changes and the resulting change in conductivity can be used to measure the rate of the reaction. These reflect the changes in the ions present in the solution and so can be used to measure the changes in concentration of the various components of the mixture</p>																									
11.4	<p>understand experiments that can be used to investigate reaction rates by:</p> <ul style="list-style-type: none"> i an initial-rate method, carrying out separate experiments where different initial concentrations of one reagent are used <p>A 'clock reaction' is an acceptable approximation of this method.</p> <ul style="list-style-type: none"> ii a continuous monitoring method to generate data to enable concentration-time or volume-time graphs to be plotted 																									
i	<p>Initial-Rate Method</p> <p>Initial rate is the time taken for a fixed amount of reactant to be used up or for a fixed amount of product to be formed</p> <p>To find out the initial rate, we can either:</p> <ol style="list-style-type: none"> 1. Draw a concentration-time graph and calculate the gradient of tangent at $t = 0$ 2. Clock reaction: Carry out a series of separate experiments where the initial concentrations of reactants are changed (one at a time) and the initial rate is measured each time and recorded <p>17 The reaction between hydrogen peroxide and iodide ions in acid conditions is known as the Harcourt-Esson reaction after the scientists who first studied its kinetics.</p> $\text{H}_2\text{O}_2(\text{aq}) + 2\text{I}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})$ <p>(a) A student carried out experiments to determine the rate equation for this reaction at 293 K.</p> <p>(ii) The student's results are shown.</p> <table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <thead> <tr> <th style="padding: 5px;">Run</th> <th style="padding: 5px;">$[\text{H}_2\text{O}_2(\text{aq})] / \text{mol dm}^{-3}$</th> <th style="padding: 5px;">$[\text{I}^-(\text{aq})] / \text{mol dm}^{-3}$</th> <th style="padding: 5px;">$[\text{H}^+(\text{aq})] / \text{mol dm}^{-3}$</th> <th style="padding: 5px;">Rate / $\text{mol dm}^{-3} \text{s}^{-1}$</th> </tr> </thead> <tbody> <tr> <td style="padding: 5px;">1</td> <td style="padding: 5px;">0.0210</td> <td style="padding: 5px;">0.0198</td> <td style="padding: 5px;">0.00105</td> <td style="padding: 5px;">0.00181</td> </tr> <tr> <td style="padding: 5px;">2</td> <td style="padding: 5px;">0.0105</td> <td style="padding: 5px;">0.0400</td> <td style="padding: 5px;">0.00105</td> <td style="padding: 5px;">0.00181</td> </tr> <tr> <td style="padding: 5px;">3</td> <td style="padding: 5px;">0.0105</td> <td style="padding: 5px;">0.0797</td> <td style="padding: 5px;">0.00099</td> <td style="padding: 5px;">0.00364</td> </tr> <tr> <td style="padding: 5px;">4</td> <td style="padding: 5px;">0.0210</td> <td style="padding: 5px;">0.0801</td> <td style="padding: 5px;">0.00201</td> <td style="padding: 5px;">0.00730</td> </tr> </tbody> </table> <p>Deduce the rate equation for this reaction. (3)</p> <p>For H_2O_2, we look at run 1 and 2, as $[\text{H}_2\text{O}_2]$ doubles, rate must be x as $[\text{I}^-]$ halves, rate must be y $xy = 1$</p> <p>Hence, H_2O_2 and I^- must be first order</p> <p>For H^+, we look at run 1 and 4, as $[\text{H}^+]$ doubles, rate must be z as $[\text{I}^-]$ quadruples, rate quadruples</p>	Run	$[\text{H}_2\text{O}_2(\text{aq})] / \text{mol dm}^{-3}$	$[\text{I}^-(\text{aq})] / \text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})] / \text{mol dm}^{-3}$	Rate / $\text{mol dm}^{-3} \text{s}^{-1}$	1	0.0210	0.0198	0.00105	0.00181	2	0.0105	0.0400	0.00105	0.00181	3	0.0105	0.0797	0.00099	0.00364	4	0.0210	0.0801	0.00201	0.00730
Run	$[\text{H}_2\text{O}_2(\text{aq})] / \text{mol dm}^{-3}$	$[\text{I}^-(\text{aq})] / \text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})] / \text{mol dm}^{-3}$	Rate / $\text{mol dm}^{-3} \text{s}^{-1}$																						
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4	0.0210	0.0801	0.00201	0.00730																						

	$4z = 4$ $z = 1$ (rate remains the same) Hence, H^+ is zero order Overall rate equation is: rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$ Unit depends on the rate equation (in this case, it is in $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)
ii	Continuous Method Only one experiment is performed, and samples of the reaction are withdrawn at regular time intervals The reaction is then stopped (quenched) and the concentration of the reactants is determined by titration Then, a concentration-time graph is drawn and after that, the successive half-life for the reactions is found out at different concentrations For this method to work the concentration of the reactants not being followed must be in large excess in the experiment so their concentrations stay virtually constant and do not affect rate
11.5	be able to deduce the order (0, 1 or 2) with respect to a substance in a rate equation, using data from: i a concentration-time graph ii a rate-concentration graph iii an initial-rate method
i	Deducing order from a concentration-time graph  <p>The figure contains three separate graphs, each with 'CONCENTRATION' on the vertical axis and 'TIME' on the horizontal axis.</p> <ul style="list-style-type: none"> FIRST ORDER: Shows a curve that decreases exponentially. Two half-lives are indicated: $t_{1/2}(1)$ and $t_{1/2}(2)$. The time interval between these two half-lives is labeled $t_{1/2}(2) - t_{1/2}(1)$. SECOND ORDER: Shows a curve that decreases more rapidly than the first-order curve. Two half-lives are indicated: $t_{1/2}(1)$ and $t_{1/2}(2)$. The time interval between these two half-lives is labeled $t_{1/2}(2) - t_{1/2}(1)$. ZERO ORDER: Shows a straight line with a negative slope. A point on the line is labeled $1/2 \text{ CONCENTRATION}$. Two half-lives are indicated: $t_{1/2}(1)$ and $t_{1/2}(2)$. The time interval between these two half-lives is labeled $t_{1/2}(2) - t_{1/2}(1)$. <p>If half-life has a constant value, then reaction is first order $\text{Rate} = k[\text{A}]$</p> <p>If half-life doubles (increases) with decreasing concentration, the reaction is second order $\text{Rate} = k[\text{A}]^2$</p> <p>If half-life decreases with decreasing concentration and the graph is a straight line with a negative gradient, then rate of reaction is constant Reaction is zero order $\text{Rate} = k$</p>

Read this together with the continuous method in 11.4ii

ii

Rate equation for rate-concentration graph is shown below



In summary,

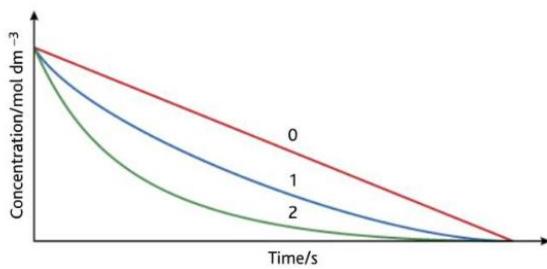


fig. 1.1.18 Graphs of zero, first and second order reactions showing how concentration changes with time.

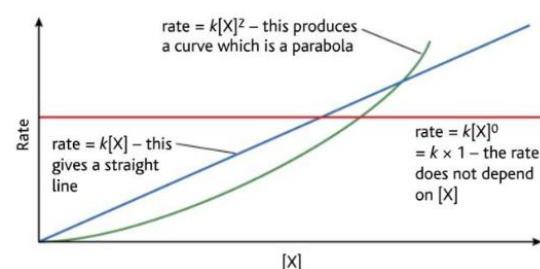
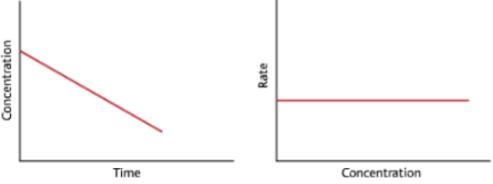
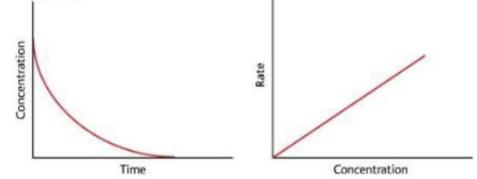
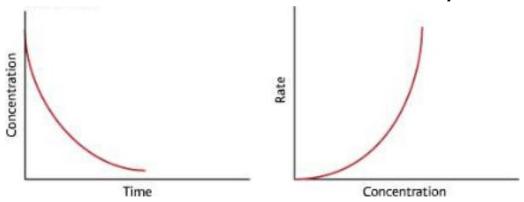


fig. 1.1.19 The variation of reaction rate with [X] for reactions which are zero, first and second order with respect to X.

iii

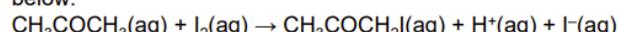
Initial rate is explained in detail in 11.4i

Basics	<p>Zero Order Reactions</p> <p>A reaction is zero order with respect to a reactant if the rate of reaction is unaffected by changes in the concentration of that reactant</p> 
	<p>First Order Reactions</p> <p>A reaction is first order with respect to a reactant if the rate of reaction is proportional to the concentration of that reactant</p> <p>This means that doubling the concentration of the reactant leads to a doubling of the rate of reaction ($\text{rate} = k[\text{A}]$)</p> <p>Hence, a plot of rate against concentration gives a straight line passing through the origin, whereas a graph of concentration of a reactant and time is a decreasing exponential graph as shown:</p> 
	<p>Second Order Reactions</p> <p>A reaction is second order with respect to a reactant if the rate of reaction is proportional to the concentration of that reactant squared</p> <p>This means that doubling the concentration of a reactant increases the rate by a factor of four: $\text{rate} = k[\text{A}]^2$</p> <p>A graph of rate against concentration squared for a second order reaction would be a straight line through the origin</p>  <p>Recall that the half-life of a first order reaction is independent of the initial concentration of the reactants, but the half-life of a second order reaction does depend on the initial concentrations of the reactants</p> <p>In second order reactions, halving the initial concentration doubles the half-life</p> <p>In other words, in second order reactions the half-life is inversely proportional to the initial concentration of the reactants. It is related to the rate constant by the following equation: $t_{1/2} = \frac{1}{k[\text{reactant}]_{\text{initial}}}$</p>
11.6	<p>understand how to:</p> <ul style="list-style-type: none"> i obtain data to calculate the order with respect to the reactants (and the hydrogen ion) in the acid-catalysed iodination of propanone ii use these data to make predictions about species involved in the rate-determining step iii deduce a possible mechanism for the reaction

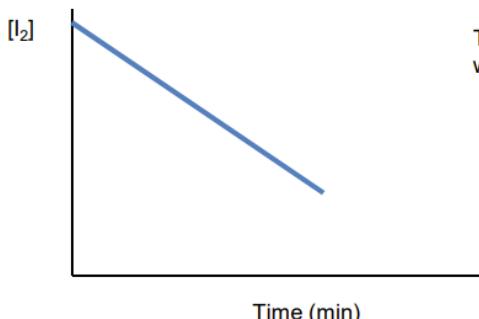
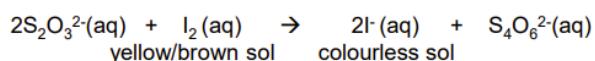
i

Investigating the rate of reaction between Iodine and propanone

Propanone reacts with iodine in acidic solution (the acid is a catalyst) as shown in the equation below.



This reaction can be followed by removing small samples from the reaction mixture with a volumetric pipette. The sample is then quenched by adding excess sodium hydrogencarbonate to neutralize acid catalyst which stops the reaction. Then the sample can be titrated with sodium thiosulphate using a starch catalyst



This reaction is zero order with respect to I_2 but 1st order with respect to the propanone and acid catalyst

The rate equation for the reaction is
Rate = $k[\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})]$

If there is a zero order reactant there must be at least two steps in the mechanism because the rate determining step will not involve the zero order reactant

The rate determining step of this reaction must therefore contain one propanone molecule and one H^+ ion forming an intermediate. The iodine will be involved in a subsequent faster step.

11.7

be able to deduce the rate-determining step from a rate equation and vice versa

The **rate-determining step is the slowest step** in a reaction

If a reactant appears in the rate-determining step, then the concentration of that reactant will also appear in the rate equation

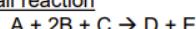
11.8

be able to deduce a reaction mechanism, using knowledge of the rate equation and the stoichiometric equation for a reaction

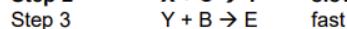
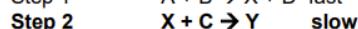
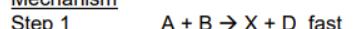
A **mechanism** is a series of steps through which the reaction progresses, often forming intermediate compounds

If all the steps are added together they will add up to the overall equation for the reaction

Example 2 overall reaction

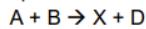


Mechanism



$$r = k[\text{X}]^1[\text{C}]^1$$

The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step



$$r = k[\text{A}]^1[\text{B}]^1[\text{C}]^1$$

The order indicates the number of molecules involved in the rate-determining step.

$$\text{rate} = k[\text{NO}_2]^2$$

Indicates that only molecules of NO_2 are involved in the rate-determining step.

11.9

understand that knowledge of the rate equations for the hydrolysis of halogenoalkanes can be used to provide evidence for S_N1 and S_N2 mechanisms for tertiary and primary halogenoalkane hydrolysis

Recall the nucleophilic substitution reaction of haloenoalkanes with hydroxide ions

Nucleophile: OH⁻ ions

Type: Hydrolysis reaction

Mechanism: nucleophilic substitution (shown in **10.9i**)



Change in functional gp. Halogenoalkane

Alcohol

Reagent: KOH or NaOH in *aqueous solution*

Conditions: Heat under reflux

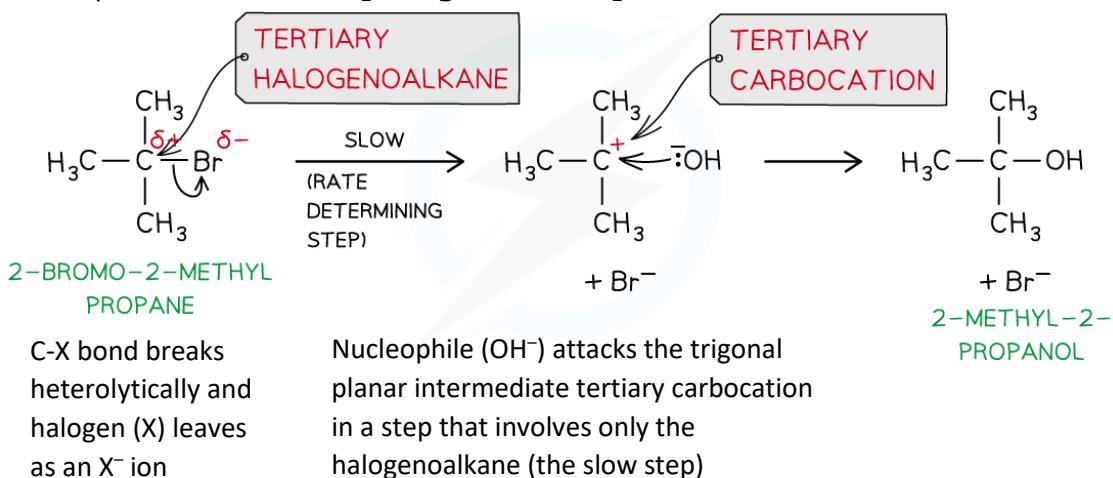
Well, this reaction can occur in either of two mechanisms- S_N1 or S_N2 depending on the structure of the halogenoalkane

S_N1 mechanism

Occurs in *tertiary* halogenoalkanes, S = Substitution N = Nucleophilic 1 = unimolecular

It is a two-step mechanism

Rate equation is: **rate = k[halogenoalkane]**

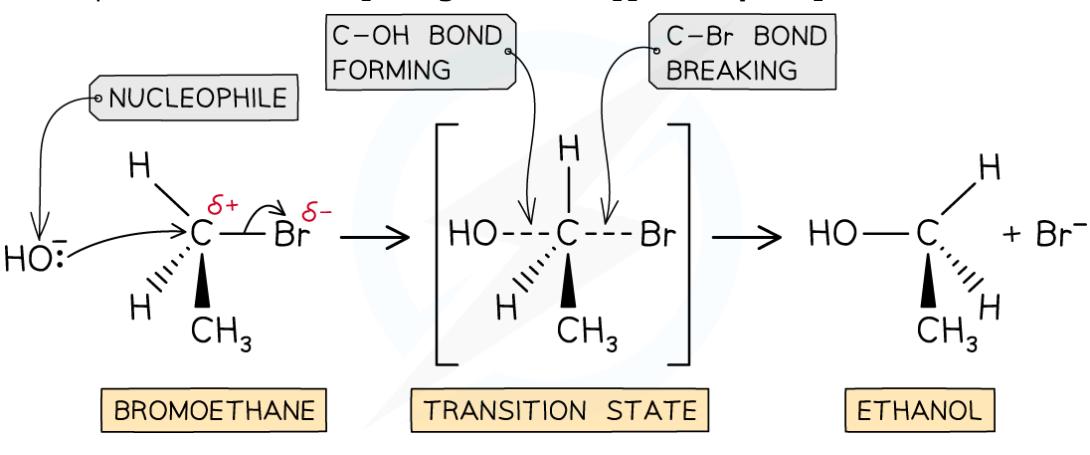


S_N2 mechanism

Occurs in *primary* haloenoalkanes, S = Substitution N = Nucleophilic 2 = bimolecular

It is a one-step mechanism

Rate equation is: **rate = k[halogenoalkane][nucleophile]**



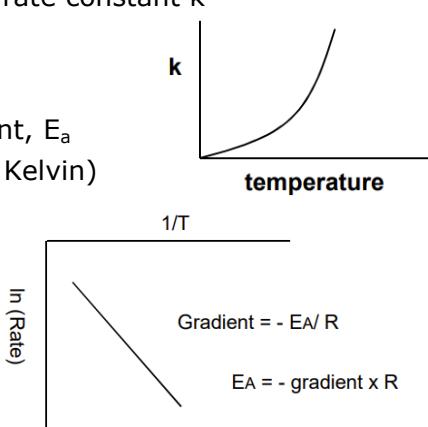
C-X bond breaks heterolytically and halogen, X leaves as an X^- ion

At the same time, nucleophile (OH^-) donates a pair of electrons to the $\delta+$ carbon atom, forming a new bond

If the original reactant was chiral then the opposite enantiomer would form

11.10 be able to use calculations and graphical methods to find the activation energy for a reaction from experimental data.

The Arrhenius equation will be given if needed.

	<p>Increasing the temperature increases the value of the rate constant k The relationship is given by the Arrhenius equation</p> $k = Ae^{-E_a/RT}$ <p>where A is the Arrhenius constant, R is the gas constant, E_a is activation energy, T is the absolute temperature (in Kelvin)</p> <p>This can be rearranged into $\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$</p> <p>If a graph of $\ln k$ is plotted against $1/T$, a straight line is obtained with a gradient of $-E_a/R$ This provides an experimental method for determining the activation energy of a reaction</p>  <p>The graph shows a straight line with a negative slope. The vertical axis is labeled $\ln(\text{Rate})$ and the horizontal axis is labeled $1/T$. The line has a negative gradient. The equation $\text{Gradient} = - E_a / R$ is written next to the line, and below it, $E_a = - \text{gradient} \times R$.</p>
11.11	<p>understand the use of a solid (heterogeneous) catalyst for industrial reactions, in the gas phase, in terms of providing a surface for the reaction</p>
	<p><u>Heterogeneous catalysts</u> are in a different phase (solid, liquid, solution or gas) to that of the reactants They are usually solids whereas the reactants are gaseous or in solution Stages of how a heterogeneous catalyst increases the rate of reaction</p> <ul style="list-style-type: none"> - The reactants adsorb onto the active sites on the surface of the catalyst - This weakens the bonds in the reactants (and reaction occurs) - The products then desorb from the surface of the catalyst <p>There will also be a higher concentration of reactants at the solid surface so leading to a higher collision frequency Two important industrial reactions include the Haber process and the Contact process</p>
11.12	<p>CORE PRACTICALS 9a and 9b</p> <p>Following the rate of the iodine-propanone reaction by a titrimetric method and investigating a 'clock reaction' (Harcourt-Esson, iodine clock).</p>

9a	<p>17 The reaction between hydrogen peroxide and iodide ions in acid conditions is known as the Harcourt–Esson reaction after the scientists who first studied its kinetics.</p> $\text{H}_2\text{O}_2(\text{aq}) + 2\text{I}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})$ <p>(a) A student carried out experiments to determine the rate equation for this reaction at 293 K.</p> <p>(i) The rate of this reaction may be obtained by adding a fixed volume of sodium thiosulfate solution and a few drops of starch solution to the reaction mixture.</p> <p>Explain how this method gives the rate of reaction. (3)</p> <p>Sodium thiosulfate reacts with the iodine formed</p> <p>When all the sodium thiosulfate that is used up has reacted, the iodine reacts with the starch giving a blue-black colour mixture</p> <p>Measure the time taken for the blue-black colour to appear</p> <p>Rate of reaction = 1/time taken for blue-black to appear</p> <p>(or) Repeat the experiment varying the concentration of a reactant and then plotting a concentration-time graph and measure initial gradient to find initial rate</p> <p>.....</p> <p>.....</p> <p>.....</p> <p>.....</p> <p>.....</p>
11.13	<p>CORE PRACTICAL 10</p> <p>Finding the activation energy of a reaction.</p> <p>Further suggested practicals:</p> <ul style="list-style-type: none"> i the reaction between marble chips and hydrochloric acid (change of mass or change in volume of gas) ii the reaction between magnesium and hydrochloric acid to determine the activation energy iii following the rate of the iodine-propanone reaction by a colorimetric method iv the catalysis by a cobalt(II) salt of potassium sodium tartrate and hydrogen peroxide v the action of the enzyme urease on urea and thiourea